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(54) **Method for producing destructureized modified starch**

(57) A method of producing a modified destructureized starch in form of a melt by heating a starch having a water content of 5 to 30 % by weight based on the starch/water composition in a closed volume to elevated temperatures thereby at elevated pressures for a time long enough to form a melt, characterised in that said process is carried out in the presence of at least one organosilane capable of reacting with a hydroxyl group. The method may be effected by conducting the heating referred to above as part of a process of injection moulding, blow moulding, extrusion, coextrusion, compression moulding or vacuum forming to produce articles of modified starch in the form of films, capsules or other shaped forms having water repellant characteristics and useful in applications as carrier for pharmaceuticals or agriculturals.

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Method for producing destructurezied modified starch

The present invention refers to a method of producing destructurezied modified starch.

It is known that natural starch which is found in vegetable products and which contains a defined amount of water, can be treated at elevated temperature to form a melt. The process is conveniently carried out in an injection molding machine or extruder. The starch is fed through the hopper onto a rotating, reciprocating screw. The feed material moves along the screw towards the tip. During this process, its temperature is increased by means of external heaters around the outside of the barrel and by the shearing action of the screw. Starting in the feed zone and continuing in the compression zone, the particulate feed becomes gradually molten. It is then conveyed through the metering zone, where homogenization of the melt occurs, to the end of the screw. The molten material at the tip can then be further treated by injection molding or extrusion or any other known technique to treat thermoplastic melts, to obtain shaped articles.

This treatment, which is described in the European Patent Application No. 84 300 940.8 (Publication No. 118 240) yields an essentially destructurezied

starch. The reason for this being that the starch is heated above the melting and glass transition temperatures of its components so that they undergo endothermic transitions. As a consequence a melting and disordering of the molecular structure of the starch granules takes place, so that an essentially destructurized starch is obtained. The expression "destructurized starch" defines starch obtained by such thermoplastic melt formation.

Articles obtained from such melts are useful and are highly compatible with nature. However, for practical purposes it is desirable that the hydrophilic nature of the destructurized starch material be diminished in such a way that it corresponds to the length of time during which the specific article should be stable against moisture before it disintegrates.

It is known to add siloxanes in many application to impart water-repellency. It has also become known to react starch with different reactive silanes in the presence of a solvent and a catalyst.

It has now been found that if water-containing starch is destructurized in the presence of a reactive organosilane there is obtained a modified destructurized starch with interesting properties and without decreased physical strength.

The present invention refers to a method of producing a modified destructurized starch in form of a melt by heating a starch having a water content of 5 to 30 % by weight based on the starch/water composition in a closed volume to elevated temperatures thereby at elevated pressures for a time long enough to form a

melt, characterised in that said process is carried out in the presence of at least one organosilane capable of reacting with a hydroxyl group.

It is surprising to note that such a silane as defined hereinbelow is practically quantitatively fixed to the starch molecule, imparting different chemical properties thereto, especially water-repellancy and compatibility with other organic or inorganic materials depending on the nature of the silane compound incorporated and fixed onto the starch.

The present invention refers also to the destructurized modified solidified starch melt obtained by this process. The present invention further refers to articles such as shaped articles, granules, powders etc. obtained from such destructurized modified starches.

The melts obtained by this process are thermoplastic melts and can be treated accordingly.

The term "starch" as used herein includes chemically essentially non-modified starch as for example generally carbohydrates of natural, vegetable origin, composed mainly of amylose and/or amylopectin. They may be extracted from various plants, examples being potatoes, rice, tapioca, corn, and cereals such as rye, oats, wheat. It further includes physically modified starch such as gelatinized or cooked starch, starch with a modified acid value (pH), e.g. where acid has been added to lower its acid value to a range of about 3 to 6. Further is included starch, e.g. potato starch, in which the divalent ions like Ca^{+2} or Mg^{+2} -ions bridging the phosphate groups have been

eliminated from this bridging function, i.e. the phosphate bridges have essentially been broken down. It further includes pre-treated starches, for example pre-extruded starches.

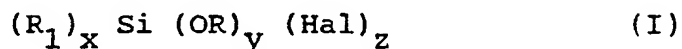
It has recently been found, that starch with a water content within the range of about 5 to about 40 % by weight based on the weight of the composition undergoes a "specific narrow endothermic transition" on heating to elevated temperatures and in a closed volume just prior to its endotherm change characteristic of oxidative and thermal degradation. This specific endothermic transition can be determined by differential scanning calorimetric analysis (DSC) and is indicated on the DSC-diagram by a specific relatively narrow peak just prior to the endotherm change characteristic of oxidative and thermal degradation. This peak disappears as soon as the mentioned specific endothermic transition has been undergone. The term "starch" includes also treated starches wherein said specific endothermic transition has been undergone.

Such starch is suitably heated for deconstructurization in a screw barrel of an extruder for a time long enough to effect deconstructurization. The temperature is preferably within the range of about 120°C to 190°C, preferably within the range of 130°C to 190°C depending on the type of starch used. For this deconstructurization, the starch material is heated preferably in a closed volume. A closed volume can be a closed vessel or the volume created by the sealing action of the unmolten feed material as happens in the screw of injection molding or extrusion equipment. In this sense the screw barrel of an injection molding

machine or an extruder is to be understood as being a closed vessel. Pressures created in a closed vessel correspond to the vapour pressure of water at the used temperature but of course pressure may be applied and/or generated as normally occurs in a screw barrel. The preferred applied and/or generated pressures are in the range of the pressures which occur in extrusion or injection molding processes and known per se, i.e. from zero to $150 \times 10^5 \text{ N/m}^2$ preferably from zero to $75 \times 10^5 \text{ N/m}^2$ and most particularly from zero to $50 \times 10^5 \text{ N/m}^2$.

The amount of reactive silane added depends of the number of reactive sites on the silane as well as on the degree of modification to be incorporated to the starch material. In general a concentration of one molecule of silane to 1000 anhydro glucose units (AGU) will already show a visible effect, although higher concentrations between 2 to 50 and preferably 5 to 20 molecules of silane to 1000 AGU are preferred. It depends on the nature of silane used and is easily optimized by the expert skilled in the art.

Preferred silanes are those of the formula



wherein

R_1 is independently alkyl ($C_1 - C_8$), substituted alkyl ($C_1 - C_4$), vinyl or phenyl, wherein the alkyl substitution is selected from chlorine, $-\text{NH}_2$, substituted amino, an unsaturated bond, or a rest carrying an epoxigroup; R is hydrogen or alkyl ($C_1 - C_4$) or acyl ($C_1 - C_4$),

preferably methyl or ethyl, Hal is halogen, preferably chlorine, bromine, preferably chlorine;

x is 1,2 or 3 preferably 1 or 2;

y is zero, 1, 2 or 3;

z is zero, 1, 2 or 3,

the sum of y + z is 1, 2, or 3, preferably 2 or 3; and

the sum of x + y + z is 4.

Preferred silanes are those wherein x is 1 or 2, preferably 1; R is methyl or ethyl, preferably methyl and R₁ is methyl, ethyl, propyl, butyl and z is zero if mainly water-repellency shall be incorporated to the starch molecule.

If other properties should be incorporated, the R₁ is preferably substituted, i.e. for additional crosslinking R₁ is substituted e.g. with an epoxy group.

Examples for such silanes are

methyltriethoxysilane, ethyltrimethoxysilane,
propyltrimethoxysilane, butyltrimethoxysilane,
chloromethyltriethoxysilane,
3-aminopropyl-trimethoxysilane,
4-aminobutyldimethylmethoxysilane,
vinyltriethoxysilane, allyltrimethoxysilane,
p-chlorophenyltriethoxysilane, as well as the
corresponding triethoxycompounds or the corresponding
dialkoxy or monoalkoxycompounds containing one resp.

two more methylgroups. Further compounds of formula (I) are 3-isocyanatopropyltriethoxysilane, 3-glycidoxypopyltrimethoxysilane, trimethylsilylacetic acid, triethylsilanol, tri-n-propylsilanol, diphenyldihydroxysilane, trimethylchlorosilane, diphenylmethylchlorosilane, tert-butyldimethylchlorosilane, triethylchlorosilane, propyldimethylchlorosilane, allyldimethylchlorosilane, wherein the alkoxysilanes with a saturated alkylrest are the preferred ones.

The silane is simply added uniformly to the starch material before transforming it into a melt by any known method, optionally using a solvent which can be evaporated. In this case special care has to be taken to keep the water content of the starch material within the prescribed range.

Optionally the pH is adjusted to lower or higher values than 7 or a catalyst like organometallic esters such as butyl-titanate which promotes the reaction between hydroxyl group and the Si-OR bond is added.

The starch/water composition to be treated according to the present invention has a preferred water content in the range of about 10 to 20 % by weight of the composition, preferably 12 % to 19 % and especially 14 % to 18 % by weight, calculated to the weight of the composition.

For destructurization, the starch/water composition according to this invention is heated to a temperature which is generally within the range of about 80 to

200°C, preferably within the range of about 120 to 190°C and especially at about 140 to 175°C.

The minimum pressure for forming the melt corresponds to the water vapour pressure produced at these temperatures. The process is carried out in a closed volume as explained above, i.e. in the range of the pressures which occur in extrusion or injection molding processes and are known per se, e.g. from zero to $150 \times 10^5 \text{ N/m}^2$ preferably from zero to $75 \times 10^5 \text{ N/m}^2$ and most particularly from zero to $50 \times 10^5 \text{ N/m}^2$.

When forming a shaped article by extrusion the pressures are preferably as mentioned above. If the melt of the destructurized starch composition according to this invention is e.g. injection molded, the normal range of injection pressures used in injection molding is applied, namely from $300 \times 10^5 \text{ N/m}^2$ to $3.000 \times 10^5 \text{ N/m}^2$ preferably $700 \times 10^5 - 2200 \times 10^5 \text{ N/m}^2$.

The starch material of the present invention may contain or may be mixed with additives such as extenders, fillers, lubricants, plasticizers, and/or coloring agents.

These additives may be added before the destructurizing step or after this step i.e. mixed with the solid granules of the destructurized starch. It mainly depends on the intended use of the destructurized starch.

Such additives are extenders of different kinds, e.g. gelatin, vegetable proteins such as sunflower protein, soybean proteins, cotton seed proteins, peanut proteins, rape seed proteins, blood proteins, egg proteins, acrylated proteins; water-soluble polysaccharides such as:

alkylcelluloses hydroxyalkylcelluloses and hydroxyalkylalkylcelluloses, such as: methylcellulose, hydroxymethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, hydroxyethylmethylcellulose, hydroxypropylmethylcellulose, hydroxybutylmethylcellulose, celluloseesters and hydroxyalkylcelluloseesters such as: celluloseacetylphthalate (CAP), Hydroxypropylmethylcellulose (HPMCP); carboxyalkylcelluloses, carboxyalkyl-alkylcelluloses, carboxyalkylcelluloseesters such as: carboxymethylcellulose and their alkalimetal salts; water-soluble synthetic polymers such as: polyacrylic acids and polyacrylic acid esters, polymethacrylic acids and polymethacrylic acid esters, polyvinylacetates, polyvinylalcohols, polyvinylacetatephthalates (PVAP), polyvinylpyrrolidone, polycrotonic acids; suitable are also phthalated gelatin, gelatin succinate, crosslinked gelatin, shellac, water soluble chemical derivatives of starch, cationically modified acrylates and methacrylates possessing, for example, a tertiary or quaternary amino group, such as the diethylaminoethyl group, which may be quaternized if desired; and other similar polymers.

Such extenders may optionally be added in any desired amount preferably up to and including 50 %, preferably

within the range of 3 % to 10 % based on the weight of all components.

Further additives are inorganic fillers, such as the oxides of magnesium, aluminum, silicon, titanium, etc. preferably in a concentration in the range of about 0.02 to 3 % by weight preferably 0.02 to 1 % based on the weight of all components.

Further examples of additives are plasticizers which include polyalkylene oxides, such as polyethylene glycols, polypropylene glycols, polyethylene-propylene glycols; organic plasticizers with low molecular weights, such as glycerol, glycerol monoacetate, diacetate or triacetate; propylene glycol, sorbitol, sodium diethylsulfosuccinate, triethyl citrate, tributyl citrate, etc., added in concentrations ranging from 0.5 to 15 %, preferably ranging from 0.5 to 5 % based on the weight of all the components.

Examples of coloring agents include known azo dyes, organic or inorganic pigments, or coloring agents of natural origin. Inorganic pigments are preferred, such as the oxides of iron or titanium, these oxides, known per se, being added in concentrations ranging from 0.001 to 10 %, preferably 0.5 to 3 %, based on the weight of all the components.

The sum of the plasticizer and water contents should preferably not exceed 25 %, and should most preferably not exceed 20 %, based on the weight of all the components.

There may further be added compounds to improve the flow properties of the starch material such as animal

or vegetable fats, preferably in their hydrogenated form, especially those which are solid at room temperature. These fats have preferably a melting point of 50°C or higher. Preferred are Triglycerides with C₁₂ -, C₁₄ -, C₁₆ -, and C₁₈ - fatty acids.

These fats can be added alone without adding extenders or plasticizers.

These fats can advantageously be added alone or together with mono- and/or diglycerides or phosphatides, especially lecithin. The mono- and diglycerides are preferably derived from the types of fats described above, i.e. with C₁₂ -, C₁₄ -, C₁₆ -, and C₁₈ - fatty acids.

The total amounts used of the fats mono-, diglycerides and/or lecithins are up to 5 % and preferably within the range of about 0.5 to 2 % by weight of the total composition.

It is further recommended to add silicon dioxide or titanium dioxide in a concentration of about 0.02 to 1 % by weight of the total composition. These compounds act as texturizing agent.

The materials described herein above form on heating and in a closed vessel a melt with thermoplastic properties, i.e. under controlled water-content and pressure conditions. Such a melt can be used in various techniques just like thermoplastic materials. These techniques include injection molding, blow molding, extrusion and coextrusion (rod, pipe and film extrusion), compression molding, to produce known articles as produced with these techniques. These

articles include bottles, sheets, films, packaging materials, pipes, rods, laminates, sacks, bags, pharmaceutical capsules, granules or powders.

Such modified starch may be used as a carrier material for active substances, and may be mixed with active ingredients such as pharmaceuticals and/or agriculturally active compounds such as insecticides or pesticides. The resulting extruded material can be granulated or worked to a fine powder.

It is further possible to treat a shaped article made from a destructure starch with the silanes of formula (I) to render its surface water-repellent. The shaped article is dipped or wetted in any suitable manner with the silane dried and heated to react the surface with the added silane, optionally in the presence of a catalyst as mentioned above.

The following examples further explain the invention.

Example 1

Natural potato starch, a lubricant/release agent (hydrogenated fat), a melt flow accelerator (lecithin), titaniumdioxide and a silane (propyltrimethoxysilan) are mixed together in the relative proportions in a powder mixer for 10 minutes so that a composition consisting of 80 parts of natural potato starch, one part of the hydrogenated triglyceride containing the fatty acid C_{18} : C_{16} : C_{14} in a ratio of 65:31:4 weight percent, 0.7 parts lecithin, 0.7 parts of TiO_2 and 0.4 parts of the silane and 17 parts water in the form of a freely flowing powder is obtained. 500 g of low molecular

saturated hydrocarbon (hexan) was added during the mixing process for better distribution of the addition. The hexan was then evaporated and the water content controlled to be at 17 % by weight of the composition. This material was then fed to the hopper of an extruder. In the screw barrel the powder was melted. The temperature within the barrel was measured to be 175°C, the average total residence time was 10 minutes and the pressure generated was equal to the vapour pressure of the moisture present in the volume of the extruder barrel. The melt was then extruded, and cut into granules of an average diameter of 2 to 3 mm. The material was hard, white with a fine foamed structure. The water content was 11.2 %, as water was allowed to escape when the melt left the extruder nozzle. The obtained granulated material was then conditioned to a water content of 17%. The material was water repellent and swam on water for 10 hours without visible disintegration.

In a further run, the melt described above was injection molded. The material was formed into a melt within the screw barrel. The temperature there was kept at 175°C, the pressure at $75 \times 10^5 \text{ N/m}^2$; the average residence time was 8 minutes. The melt was injected into a mold so that test pieces were produced suitable for testing their physical properties (stress/strain behaviour) on an INSTRON tensile listing apparatus. The samples were conditioned at 13.5 % water content and measured at room temperature using an extension rate of 10 mm per minute. The stress/strain values did not differ from the values obtained without the addition of the silane. The water stability of the test pieces was very much improved.

Example 2

600 g of native potato starch were suspended in 700 ml of 0.2N HCl and stirred for 10 minutes. the suspension was filtered and the starch washed on the filter three times with 200 ml portions of 0.2N HCl. The starch was again suspended in 500 ml 0.2N HCl, stirred again for 10 minutes, filtered, washed three times with 200 ml portions of 0.2N HCl.

After this treatment with HCl the excess of acid was removed by washing with demineralized (deionized) water in following way: the starch was washed twice with 200 ml portions of deionized water and then suspended in 500 ml of deionized water. This washing procedure with deionized water (to remove excess acid) was repeated twice to get the starch free of HCl. This was controlled by adding silver nitrate to the washing water. When there was no more silver chloride precipitating in the washing water, the washing was completed. The washed starch was pressed on the filter and dried in a conditioning room (25°C, 40 % RH) until it equilibrated at about 17.0 % H₂O. In another run the wet starch was treated in a fluidized bed with blowing air at 50°C until the moisture content of starch reached 17 % by weight (as checked by periodical sampling of the starch).

Analysis was carried out before and after the acid washing of starch and result obtained showed that the Ca⁺²-ions originally present were essentially removed. This starch was then treated according to Example 1 at a temperature of 130°C and used instead of the native starch used there. Analogous results were obtained.

Example 3

Natural potato starch, a lubricant/release agent (hydrogenated fat) and a melt flow accelerator (lecithin), titanium dioxide are mixed together in the relative proportions in a powder mixer for 10 minutes so that a composition consisting of 80,6 parts of natural potato starch, one part of the hydrogenated triglyceride containing the fatty acids C_{18} : C_{16} : C_{14} in a ratio of 65:31:4 weight percent, 0.7 parts lecithin, 0.7 parts of titanium dioxide and 17 parts water in the form of a freely flowing powder is obtained. This material was then fed to the hopper of an extruder. In the screw barrel the powder was melted. The temperature within the barrel was measured to be 165°C, the average total residence time was 12 minutes (approx. 10 minutes heating time, approx. 2 minutes in molten state) and the pressure generated was equal to the vapour pressure of the moisture present in the volume of the extruder barrel. The melt was then extruded, cooled and grinded to a fine free flowing powder. 100 g of this powder was then mixed with 3.5 g of methyltrimethoxysilane using a low molecular saturated hydrocarbon solvent and injection molded to test pieces as described in Example 1. Very good results were obtained.

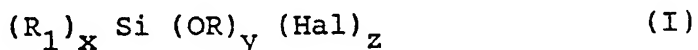
The term "rest" is used in this specification to represent a chemical group or radical.

Claims

1. A method of producing a modified destructureized starch in form of a melt by heating a starch having a water content of 5 to 30 % by weight based on the starch/water composition in a closed volume to elevated temperatures thereby at elevated pressures for a time long enough to form a melt, characterised in that said process is carried out in the presence of at least one organosilane capable of reacting with a hydroxyl group.
2. A method according to claim 1, wherein said starch is selected from chemically essentially non-modified starch being carbohydrates of natural, vegetable origin composed mainly of amylose and/or amylopectin, preferably potatoes, rice, tapioca, corn, rye, oats, wheat; physically modified starch; starch with a modified acid value (pH); starch, in which the divalent ions bridging the phosphate groups have been eliminated from this bridging function; and/or pre-extruded starches.
3. A method according to the claims 1 or 2, wherein said starch is heated for destructureization in a closed volume for a time long enough to effect destructureization to a temperature within the range of about 120°C to 190°C, preferably within the range of 130°C to 190°C.
4. A method according to anyone of the claims 1 to 3, wherein pressure is applied in the range of from zero to $150 \times 10^5 \text{ N/m}^2$, preferably from zero

to $75 \times 10^5 \text{ N/m}^2$ and particularly from zero to $50 \times 10^5 \text{ N/m}^2$.

5. A method according to anyone of the claims 1 to 4, wherein the amount of reactive silane is within a concentration of one molecule of silane to 1000 anhydro glucose units (AGU), preferably between 2 to 50 and preferably 5 to 20 molecules of silane to 1000 AGU.
6. A method according to anyone of the claim 1 to 5, wherein the silane added corresponds to the formula



wherein

R_1 is independently alkyl ($C_1 - C_8$), substituted alkyl ($C_1 - C_4$), vinyl or phenyl, wherein the alkyl substitution is selected from chlorine, $-NH_2$, substituted amino, an unsaturated bond or a rest carrying an epoxigroup; R is hydrogen or alkyl ($C_1 - C_4$) or acyl ($C_1 - C_4$), preferably methyl or ethyl, Hal is halogen, preferably chlorine, bromine, preferably chlorine;

x is 1,2 or 3 preferably 1 or 2;

y is zero, 1,2, or 3;

z is zero, 1,2, or 3

the sum of $y + z$ is 1,2, or 3, preferably 2 or 3; and

the sum of $x + y + z$ is 4.

7. A method according to claim 6, wherein silanes of the formula (I) are used wherein x is 1 or 2, preferably 1; R is methyl or ethyl, preferably

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methyl and R_1 is methyl, ethyl propyl, butyl;
and z is zero.

8. A method according to anyone of the claims 1 to 7, wherein the pH is adjusted to lower or higher values than 7 or a catalyst which promotes the reaction between hydroxyl groups and the Si-OR bond is added.
9. A method according to anyone of the claims 1 to 8, wherein the starch/water composition has a water content in the range of about 10 to 20 % by weight of the composition, preferably 12 % to 19 % and especially 14 % to 18 % by weight, calculated to the weight of the composition.
10. A method according to anyone of the claims 1 to 9, wherein the starch/water composition according to this invention is heated to a temperature within the range of about 80 to 200°C, preferably within the range of about 120 to 190°C and especially at about 140 to 175°C.
11. A method according to anyone of the claims 1 to 10, wherein the starch composition contains extenders, fillers, lubricants, plasticizers and/or coloring agents.
12. A method according to claim 11 , characterized in that there is added at least one extender or a mixture or extenders within the range of up to 50 %, preferably within the range of 3 % to 10 %, based on the weight of all components.
13. A method according to claims 11 or 12, characterized in that there is added at least one inorganic filler or a mixture of such

fillers in a concentration of about 0.02 to 3 %, preferably 0.02 to 1 %, by weight of all components.

14. A method according to anyone of the claims 11, to 13, wherein there is added a plasticizer within the range of about 0.5 to 15 %, preferably 0.5 to 5 % by weight of all components.
15. A method according to anyone of the claims 11 to 14, wherein a coloring agent is added in a concentration of about 0.001 to 10 %, preferably 0.5 to 3 % by weight of all components.
16. A method according to anyone of the claims 11 to 15, wherein a plasticizer is added and the sum of the plasticizer and water contents does not exceed 25 %, and preferably does not exceed 20 %, by weight of all components.
17. A method according to anyone of the claims 1 to 16, wherein there is added to the starch at least one active ingredient selected from pharmaceuticals and/or agriculturally active compounds.
18. The melt obtained according to anyone of the claims 1 to 17.
19. The solidified destructured starch obtained by cooling the material obtained according to claim 18.
20. The use of modified starch obtained as claimed in anyone of the claims 1 to 19 as carrier material for active ingredients, preferably as

carrier materials for pharmaceuticals, and/or agriculturally active substances.

21. The process of shaping destructured starch according to anyone of the claims 1 to 19, under controlled water content and pressure conditions as a thermoplastic melt wherein said shaping process is at least one member selected from the class consisting of injection molding, blow molding, extrusion and coextrusion, compression molding or vacuum forming.
22. Shaped articles produced from a composition obtained by the method as claimed in anyone of the claims 1 to 19.
23. The articles of claim 21, wherein said articles have been shaped as bottles, sheets, films, packaging materials, pipes, rods, laminates, sacks, bags or pharmaceutical capsules, granules or powders.
24. A water-repellent article made from destructured starch obtained by treating its surface with a silane compound according to the claims 6 to 8.

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